

Density Functional Theory (DFT) and Natural Bond Orbital (NBO) Analysis of Intermolecular Hydrogen Bond Interaction in "Phosphorylated Nata de Coco - Water"

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ABSTRACT

This study aims to study the conformation, the hydrogen bond network, and the stabilities of all the possible intermolecular interactions in phosphorylated nata de coco membrane with water (NDCF-(H₂O)_n, n = 1-5). Analysis of Natural Bond Orbital (NBO) was performed to measure the relative strength of the hydrogen bonding interactions, charge transfer, particularly the interactions of n-σ* O-H and to take into account the effect on the stabilities of the molecular structure. All calculation were performed using Density Functional Theory (DFT) method, at B3LYP functional level of theory and 6-311 G** basis set. The charge transfer between the lone pair of a proton acceptor to the anti-bonding orbital of the proton donor provides the substantial to the stabilization of the hydrogen bonds. Interaction between NDCF and (H₂O)₅ was strongest with the stabilization energy of 37.73 kcal/mol, that indicate the ease of donating lone pair electrons. The contributions of each hydrogen bond to the stability of the complex have been analyzed.

Keywords: proton transfer; hydrogen bonds; phosphorylated nata de coco; NBO

ABSTRAK

Penelitian ini bertujuan untuk mempelajari konformasi, jaringan ikatan hidrogen, dan stabilitas dari semua interaksi molekul yang mungkin, antara membran nata de coco terfosfatasi dengan air (NDCF-(H₂O)_n, n = 1-5). Perhitungan menggunakan Fungsional B3LYP dengan basis set 6-311 G**. Analisis menggunakan Teori ikatan orbital alami (Natural Bond Orbital, NBO) dilakukan untuk mengukur kekuatan relatif dari interaksi ikatan hidrogen, transfer muatan (khususnya interaksi n-σ* O-H) dan untuk memperhitungkan efeknya pada stabilitas struktur molekul. Transfer muatan antara pasangan elektron bebas (lone pair) dari akseptor proton ke orbital anti ikatan dari donor proton memberikan stabilisasi besar terhadap ikatan hidrogen. Interaksi antara NDCF dengan (H₂O)₅ ditemukan paling kuat dengan energi stabilisasi 37,73 kkal/mol, menandakan kemudahan dalam mendonorkan lone pair elektron. Kontribusi dari masing-masing ikatan hidrogen untuk stabilitas kompleks NDCF-(H₂O)_n telah dianalisis.

Kata Kunci: transfer proton; ikatan hidrogen; nata de coco terfosfatasi; NBO

INTRODUCTION

The human needs, especially for energy, are increasing over the time in line with the increasing number of population and their life development. The energy needed is no longer met by the natural resources available. Since the fulfillment of the energy needed still relies on natural resources originated from fossil. The limitation of fossil resources availability in nature and its problem of renewability insist them to find other alternative energy sources. A new kind of energy which has a great potential to substitute fossil fuel is fuel cell. Fuel cell technology has been developed worldwide in recent years since it has excellences such as to be highly efficient and environmentally-friendly energy source (low emission). Fuel cell is a kind of alternative

energy sources working on the principles of electrochemical cell, which can directly change the chemical energy contained in the fuel like hydrogen to be electrical energy [1-3].

Many kinds of fuel cells have been developed. The most very promising fuel cell which is very efficient, environmentally friendly, and using polymer membrane as its electrolyte is PEMFC (Proton Exchange Membrane Fuel Cell) [4-7]. The membrane is functioning to transport cations are hydrogen ions (protons) in an electrolyte membrane from anodes to cathodes. But the membrane cannot transport any electron [8-9]. Nowadays, Nafion is an electronic membrane which is widely used for PEMFC. Unfortunately, Nafion has some limitations such as, among others, spending expensive cost (600–1000

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\$/m²) and probably to be dehydrated when used in a high temperature [10] which can reduce proton conductivity in the high temperature [11-13].

These become the basis of seeking a new alternative membrane which is expected to be used in PEMFC with a lower production cost. One of membranes which have a potential to be used in PEMFC is phosphorylated nata de coco membrane. Studies' findings showed that proton conductivity of phosphated nata de coco membrane is almost close to Nafion 117's conductivity which is of 1.20×10^{-2} S/cm [14]. Nata de coco is selected for this study since it relatively spends low cost, easily to obtain and has good mechanical properties. In addition, phosphorylated nata de coco has many hydroxyl and (-PO(O•••H)₂) groups so that it is potentially to be a polyelectrolyte membrane. Phosphorylated nata de coco has hydrophobic and hydrophilic domains which allow the occurrence of proton transfer. Its membrane has groups of hydroxyl and phosphonate which can form hydrophilic pathways through its hydrogen bonds. This causes the proton to be easily to cross the membrane matrix. Like in Nafion, sulphonate groups existing can form hydrophilic pathways to let the proton cross [12]. In addition, the polarity and the negative charge of phosphonate groups may transfer protons appropriately. The occurrence of proton transfer is showed by the existence of hydrogen bonds formed from phosphonate groups. The easiness of proton transfer process can be seen by the hydrogen bonds formed by seeing the occurrence of charge transfer inter-lone pairs from proton's acceptor to the anti-bonding orbitals from proton donor [15].

Theoretical reviews about proton transfer associated with the formation of hydrogen bonds have been done like, among others, NBO-analysis on the ratio of acceptor orbitals in both inter- and intramolecular OHO hydrogen bonds which shows the major different of both of them. In intramolecular OHO hydrogen bonds, protons are transferred to one of accepting orbitals which determines the direction of hydrogen bonds. While in intermolecular one, proton transfer is not determined by the direction of electron pairs' acceptor, since protons are transferred in a comparable number for both lone pairs from the acceptors [16]. Besides, the transfer of protons and electrons in a phenol-imidazol-base system and proton transfer in perfluorosulphonate acid ionomer are determined using DFT/B3LYP method which can provide a high accuracy in explaining the process of proton transfer. The natures of hydrogen bonds system and disassociation level are crucial factors to determine the amount of energy barrier against proton transfer in perfluorosulphonate acid ionomer. [17-18]. The NBO-analysis also describes proton transfer mechanism in the reaction of amino acid through a rearrangement of electron density. In addition, the hydrogen bonds formed

can be shown through the existence of donor and acceptor of electron lone pairs. In the phosphonate groups, there are O-atoms which are able to donate their electron lone pairs and there are H-atoms which may function as acceptors of those electron lone pairs. This ability of the donor and acceptor is what may cause the occurrence of proton transfer in phosphorylated nata de coco. Based on that, this study tried to review the process of proton transfer in the interaction of p phosphorylated nata de coco and water molecules based on NBO-analysis. The Natural Bond Orbital Analysis is used to describe the potential of proton transfer based on hydrogen bonds formed during the interaction between both inter and intramolecular phosphorylated nata de coco and *n* H₂O, by considering all possible interaction between proton donor and acceptor.

COMPUTATIONAL METHOD

All electronic structural calculation of both inter- and intramolecular interaction of phosphorylated nata de coco (NDCF) and water molecules were done using Gaussian09 program [19]. The calculation were performed using the density functional theory (DFT) and Becke's three-parameter functional (B3LYP) method with the 6-311G (d) basis set, and then be corrected for ZPE and BSSE. B3LYP is a function which is widely used in many studies and has shown good results when compared by experimental results [20]. The use of a combination of DFT method with B3LYP theory level (Becke, 3-parameter Lee, Yang and Parr) can be done to reflect a polymer's ability to transfer its protons [21-22]. NBO computation was done to analyze the probability of interaction between non-Lewis acceptors and to compute their respective energies. Interactions in NDCF-*n*H₂O may be both intermolecular or intramolecular interaction.

Interaction of electron delocalization can be reflected quantitatively using stabilizing energy ($E^{(2)}$) which is estimated based on the theory of "the Second Order Perturbation". The stabilizing energy can be formulated as follows:

$$E^{(2)} = \Delta E_{i,j} = q_i \frac{F_{ij}^2}{E_i - E_j} \quad (1)$$

where $E^{(2)}$ is orbital stabilizing energy, q_i shows the occupancy of donating orbitals, E_i and E_j , respectively, are energy of NBO donor and acceptor, and F_{ij} is Fock matrix element between NBO orbitals *i* and *j* orbitals [20].

In NBO-analysis on hydrogen bonds system, the most significant thing is the charge transfer between lone pairs (LP) from proton acceptor and of anti-bonding from proton donor. While $E^{(2)}$, between LP of Y

atom and σ^* of X-H bonds is correlated with X-H...Y interaction intensity and may give qualitative description of its contribution to the total energy of NDCF- n H₂O interaction [23].

RESULT AND DISCUSSION

NBO-Analysis

The NBO calculation of all interaction of NDCF (two monomers = dimer) and n water molecules has been done at the B3LYP level with the 6-311G (d) basis set and the data of non-Lewis acceptors and donors, as well as the stabilizing energy of interaction involved in hydrogen bonds are reported in Table 1. The NBO-analysis, stabilizing energy ($E^{(2)}$) is used to characterize the interaction between occupied and unoccupied NBO-typed Lewis orbitals which contributes to the electron delocalization from bonding (BD) or lone pair orbitals (LP) to anti-bonding orbitals (BD*) [24]. In addition, the stabilizing energy ($E^{(2)}$) is also used to characterize the interaction of hydrogen bonds between lone pairs (LP (Y)) from a Y-atom and anti-bonding orbitals (BD* (X-H)).

The NBO-analysis on the interaction of NDCF dimer and water molecules showed that there were two interactions of both inter- and intramolecular electron lone pairs. Intermolecular interaction between lone pairs donating orbital of O₃₁ and O₅₂-H₅₄ (LP (2) O₃₁ → σ^* (O₅₂-H₅₄)) anti-bonding orbital gave a stabilization of 11.24 kcal/mol. While interaction between lone pairs orbital donor of O₅₆ and O₄₇-H₄₉ (LP (2) O₅₆ → σ^* (O₄₇-H₄₉)) anti-bonding orbital gave a stronger stabilization of 21.38 kcal/mol.

The interaction NDCF dimer with two water molecules LP (2) O₅₆, LP (3) O₅₁ and LP (2) O₅₉ participated as donors, while σ^* (O₄₇-H₄₉), σ^* (O₅₉-H₆₁) and σ^* (O₅₃-H₅₅) as acceptors. Such interaction was a consequence of intermolecular charge transfer which caused a stabilization of hydrogen bonds with respective stabilizing energies were 24.89; 7.87 and 19.34 kcal/mol. In addition, there was a NDCF-(H₂O)₂ intermolecular interaction where LP(2) O₃₁ participated as donor and σ^* (O₅₂-H₅₄) as acceptor with a stabilizing energy of 11.66 kcal/mol.

The O-H...O hydrogen bonds largely contribute to the stability of NDCF-(H₂O)₅ molecular arrangement was the intermolecular hyperconjugation interaction of

Table 1. Second-order perturbation stabilization energies of the H-bonded in phosphorylated nata de coco + n H₂O

NDCF+ n H ₂ O	Donor (i)	Acceptor (j)	$E^{(2)}$ (kcal/mole)	Distance, r (Å)
1	LP (2) O56	σ^* (O ₄₇ -H ₄₉)	21.38	H49 ---- O56 1.716
	LP (2) O31	σ^* (O ₅₂ -H ₅₄)	11.24	H54 ---- O31 1.807
2	LP (3) O51	σ^* (O ₅₉ -H ₆₁)	7.87	H61 ---- O51 1.902
	LP (2) O 56	σ^* (O ₄₇ -H ₄₉)	24.89	H49 ---- O56 1.683
2	LP (2) O 59	σ^* (O ₅₃ -H ₅₅)	19.34	H55 ---- O59 1.751
	LP (2) O 31	σ^* (O ₅₂ -H ₅₄)	11.66	H54 ---- O31 1.798
3	LP (3) O 51	σ^* (O ₅₉ -H ₆₁)	5.12	H61 ---- O51 1.948
	LP (3) O46	σ^* (O ₆₂ -H ₆₄)	7.49	H64 ---- O46 1.878
	LP (2) O 56	σ^* (O ₄₇ -H ₄₉)	22.25	H49 ---- O56 1.712
	LP (2) O 59	σ^* (O ₅₃ -H ₅₅)	22.12	H55 ---- O59 1.712
4	LP (2) O 62	σ^* (O ₄₈ -H ₅₀)	22.22	H50 ---- O62 1.715
	LP (3) O 51	σ^* (O ₅₉ -H ₆₁)	7.29	H61 ---- O51 1.883
4	LP (3) O 46	σ^* (O ₆₂ -H ₆₄)	7.09	H64 ---- O46 1.898
	LP (2) O31	σ^* (O ₆₅ -H ₆₆)	14.94	H66 ---- O31 1.728
	LP (2) O 56	σ^* (O ₄₇ -H ₄₉)	22.8	H49 ---- O56 1.707
	LP (2) O 59	σ^* (O ₅₃ -H ₅₅)	20.1	H55 ---- O59 1.741
	LP (2) O 62	σ^* (O ₄₈ -H ₅₀)	22.79	H50 ---- O62 1.706
	LP (2) O 65	σ^* (O ₅₂ -H ₅₄)	36.53	H54 ---- O65 1.588
	LP (3) O 51	σ^* (O ₃₁ -H ₄₃)	8.48	H43 ---- O51 1.808
	LP (1) O 48	σ^* (O ₅₆ -H ₅₈)	5.04	O48 ---- H58 1.975
	LP (2) O 31	σ^* (O ₆₅ -H ₆₆)	13.4	O31 ---- H66 1.795
	LP (1) O 46	σ^* (O ₆₈ -H ₇₀)	8.65	O46 ---- H70 1.747
5	LP (1) O 51	σ^* (O ₅₉ -H ₆₁)	2.76	O51 ---- H61 1.868
	LP (2) O 56	σ^* (O ₄₇ -H ₄₉)	22.92	O56 ---- H49 1.707
	LP (2) O 59	σ^* (O ₅₃ -H ₅₅)	19.12	O59 ---- H55 1.756
	LP (2) O 62	σ^* (O ₄₈ -H ₅₀)	37.73	O62 ---- H50 1.573
	LP (2) O 65	σ^* (O ₅₂ -H ₅₄)	37.52	O65 ---- H54 1.580
	LP (2) O 68	σ^* (O ₆₂ -H ₆₄)	24.28	O68 ---- H64 1.682
	LP (2) O 6	σ^* (O ₃₁ -H ₄₃)	7.64	O6 ---- H43 1.846

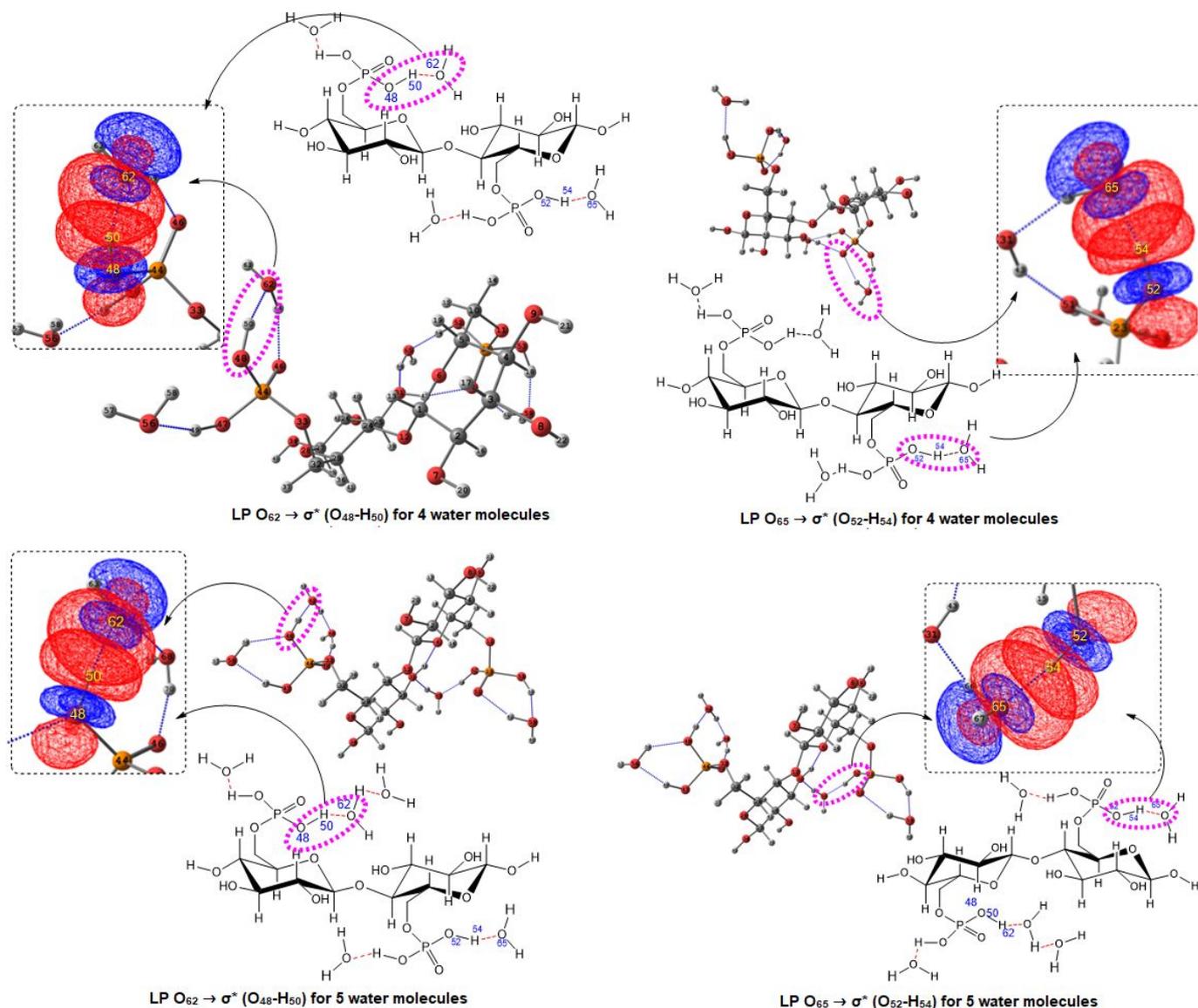


Fig 1. NLMO lone pair orbital proton donor and proton acceptor dimer NDCF with *n* molecules of water NLMO

LP (2) O₆₂ → σ* (O₄₈-H₅₀) which about 37.73 kcal/mol. A strongest interaction between NDCF with (H₂O)₅ was found in the bonds of NDCF and water with a consideration to the intermolecular relationship and the greatest energy among all interaction in NDCF-*n*H₂O. The amount of such energy indicated the easiness of electron lone pair donation. The existence of electron lone pair donation indicated the existences of hydrogen bonds of inter-phosphate groups with water molecules which was able to transfer proton towards other phosphate groups. The significant stabilization energy of 19 from 29 the NDCF-(H₂O)₁₋₅ interaction (11.24-37.73 kcal/mol), with a hydrogen bond length 1.57-1.98 Å, indicate a strong hydrogen bonded system (Table 1)

[15]. The stronger intermolecular hydrogen bonding, the easier the intermolecular transfer of protons [25].

Such findings then be proven by observing the extent to which the overlap between LP(2)) O₆₂ → σ* (O₄₈-H₅₀) lone pairs orbitals and LP(2)) O₆₅ → σ* (O₅₂-H₅₄) orbital happened. As shown in Fig. 1, LP(2) in O₆₅ had a quite great overlap with σ* (O₅₂-H₅₄) orbital, a proper orientation which caused beneficial overlap for the two orbitals. The overlap indicates a high stabilization energy interaction between 22.79 to 37.73 kcal/mol due to the hyperconjugation interaction from LP (O)_{H₂O} → σ* (O-H)_{NDCF} resulting from intermolecular interaction [25].

Table 2. Quantum parameters for phosphorylated nata de coco + *n* H₂O

NDCF + <i>n</i> H ₂ O	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE = E _{LUMO} - E _{HOMO} (eV)	A (eV)	I (eV)	X (eV)
0	-7.479	0.174	7.653	7.479	-0.174	3.652
1	-7.377	-0.199	7.178	7.377	0.199	3.788
2	-7.369	-0.229	7.140	7.369	0.229	3.799
3	-6.864	0.052	6.916	6.864	-0.052	3.406
4	-6.990	0.186	7.176	6.990	-0.186	3.402
5	-7.162	0.197	7.358	7.162	-0.197	3.483

Molecular Orbitals

The quantum chemical parameters which are associated with molecular electronic structure are electron affinity (A) and ionization potential (I) of corresponding molecules with energies of HOMO and LUMO. In a simple molecular orbital theoretical approach, based on Koopmann theorem, HOMO energy (E_{HOMO}), related to ionization energy (I, equation 2) and LUMO energy (E_{LUMO}) has been used to estimate the electron affinity (A, equation 3).

$$I = -E_{\text{HOMO}} \quad (2)$$

$$A = -E_{\text{LUMO}} \quad (3)$$

From this value, the electronegativity (χ) [26], can be obtained from the equation 4:

$$\chi = \frac{(I + A)}{2} \quad (4)$$

HOMO energy value shows molecular ability to donate electron in which a value higher than E_{HOMO} value implies the increase of molecular ability to donate electron to the acceptor. While E_{LUMO} shows molecular ability to receive electron. A molecule having low E_{LUMO} has ability to receive more electrons.

The energy gaps reflect chemical activities of molecules and describe the final stabilization of NDCF-(H₂O)₅ molecules [27]. According to Table 2, the greatest energy gaps (ΔE) is in the addition of five water molecules. This shows that the molecules have high stabilization.

CONCLUSION

The charge transfer between the lone pair of a proton acceptor to the anti-bonding orbital of the proton donor provides the substantial to the stabilization of the hydrogen bonds. The interaction between LP(2) O₆₂ → σ* (O₄₈-H₅₀) and NDCF-(H₂O)₅ was found as the strongest one with a stabilizing energy of 37.70 kcal/mol. This amount of energy encodes the easiness of electron lone-pairs donation. The existence of electron lone-pairs donation shows the existence of hydrogen bonds between phosphate groups and water molecules which is able to transfer protons towards other phosphate groups.

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